mental determination of this moment is somewhat difficult due to the small percentage of Cu(II) present (5.7%). The measurements for the diamagnetic complex, $[Hg(OMPA)_3](ClO_4)_2$, are included for comparison. The magnetic moments of $[Cu(OMPA)_2][CuBr_4]$ and $[Cu(OMPA)_2][CuCl_4]$ are in excellent agreement with the calculated value for two unpaired electrons. The magnetic moment of $[Fe(OMPA)_3](ClO_4)_3$ is slightly higher than the spin-only value for five unpaired electrons. This is further evidence for the weak field property of OMPA that was noted earlier in complexes of Ni(II) and Co(II).[2]

The present work provides evidence that OMPA is not only a versatile ligand, but also a ligand that can fulfill the maximum coordination number of a metal ion even though spectral evidence (colorless Cu(II), low *Dq* parameter toward Ni(II)[2]) indicates weak bonding.

The Synthesis and Chemistry of a Novel Macrocyclic Schiff Base Dihydrogen Perchlorate by Condensation of $Fe(en)_3^{2+}$ with Acetone

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Abstract: A new quadridentate Schiff base dihydrogen perchlorate has been prepared by means of the reaction of $[Fe(en)_3](ClO_4)_2$ with acetone. The physical and chemical evidence indicates that this compound is a protonated Schiff base having a cyclic structure. The two protons of the protonated macrocycle may be displaced by metal ions in basic solution. The Schiff base dihydrogen perchlorate has proved to be a very useful intermediate in the preparation of macrocyclic complexes of several metals.

In recent years there have been a number of different kinds of condensation reactions reported in which a transition metal ion functions as a template, holding the condensing ligand molecules in a suitable orientation to facilitate the formation of products.[1-3] Curtis and co-workers[3-5] have reported and extensively investigated the formation of macrocyclic Schiff base amine complexes of Cu(II) and Ni(II) by means of the template condensation of acetone with an amine complex of the metal (eq 1). Analogous reactions for

$$[M(en)_n](ClO_4)_2 + 4CH_3COCH_3 \longrightarrow [M(C_{16}H_{32}N_4)](ClO_4)_2 + (n\text{-}2)en + 4H_2O \quad (1)$$

Co(II) and Fe(II) amines have not been reported. The chemistry of the macrocyclic Schiff base complexes of the latter two metals is of particular interest owing to their similarity with such biologically important systems as vitamin B_{12} and hemoglobin.

One of the most interesting features of the chemistry of the macrocyclic Schiff base complexes, $M(C_{16}H_{32}N_4)^{2+}$, of Ni(II) and Cu(II) is their unusual inertness to hydrolysis or substitution even in the presence of strong mineral acids or CN^-.[3-6] This is distinctly in contrast to the usual substitution lability of most Ni(II) and Cu(II) amine complexes[7] and is reminiscent of the behavior of the corresponding metalloporphyrin complexes.[8] It is to be noted, however, the Curtis' macrocyclic Schiff base amine complexes do differ from the metalloporphyrins in that Schiff base amine ligands cannot derive any stability from a conjugated system of double bonds. In fact the macrocyclic Schiff base amine ligands are more closely related to the well-known aliphatic Schiff bases than to the porphyrins. Since aliphatic Schiff bases are generally hydrolyzed rapidly by aqueous acid,[9] we have been surprised that a stable macrocyclic Schiff base dihydrogen perchlorate, $C_{16}H_{32}N_4 \cdot 2HClO_4$, can be obtained in excellent yield from reaction 1 when M = Fe(II). We have been primarily interested in using this Schiff base dihydrogen perchlorate (I) as an intermediate in the preparation of macrocyclic complexes of several metal ions. The preparation, synthetic uses, and some preliminary observations of the chemistry of this Schiff base dihydrogen perchlorate are the subject of this report.

Experimental Section

Infrared spectra were determined from Nujol and hexachlorobutadiene mulls of the dry solids, using both the Perkin-Elmer Models 137 and 237 spectrometers. Visible and ultraviolet absorption spectra were measured with a Cary 14 recording spectrometer. A Varian A-60 high-resolution nmr spectrometer was used to obtain the proton resonance spectra.

Elemental analyses were performed by Spang and/or Schwartzkopf microanalytical companies. Schwartzkopf Microanalytical Company determined molecular weights in pyridine using a vapor pressure osmometer.

Preparations. 5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene Dihydrogen Perchlorate, $C_{16}H_{32}N_4 \cdot 2HClO_4$. This preparation seemed to be very sensitive to the presence of

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[8] J. E. Falk and J. N. Phillips in "Chelating Agents and Metal Chelates," F. P. Dwyer and D. P. Mellor, Ed., Academic Press Inc., New York, N. Y., 1964, Chapter 10.

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Table I. Prominent Infrared Absorption Frequencies of $[C_{16}H_{34}N_4](ClO_4)_2$ and the Analogous Schiff Base Complexes of Ni(II), Cu(II), Zn(II), Co(II), and Co(III)

[A]· 2HClO$_4$[a]	[NiA] (ClO$_4$)$_2$[b]	[NiA]- (ClO$_4$)$_2$[c]	[CuA]- (ClO$_4$)$_2$[b]	[ZnACl(H$_2$O)]- (ClO$_4$)$_2$[b]	[CoA]- (ClO$_4$)$_2$[c]	[CoACO$_3$]- ClO$_4$[b]	Assignments[d]
				3500 mb			O—H stretch
3145 s, b	3170 m, sp	3175 m, sp	3205 s, sp	3260 s, sp	3200 m, sp	3250 m, sp	N—H stretch
2978 w, sh	2986 m	2990 m	2985 m	2980 m	2990 m	2970	
2910 m	2932 m	2932 m	2920 m	2940 m	2930 m	2930 mb	C—H stretch
2850 w, sh				2870 sh			
1670 s, sp	1662 s, sp	1665 s, sp	1675 s, sp	1670 s, sp	1670 s, sp	1675 vs, b[e]	C═N stretch
						1636 vs, sp[e]	
1544 s							NH$_2$ asym, bend
1475 sh	1465 s	1468 m	1475 m	1480 w	1470 m	1464 m	
1455 s	1442 s	1458 m	1448 m	1450 s, b	1448 m	1448 s	
1433 sh	1412 m	1410 m	1420 m	1420 m	1418 m	1422 m	CH$_2$ and CH$_3$
1405 m	1400 m	1400 sh	1400 m		1400 sh	1400 m	deformation
1380 s, b	1378 s	1384 s	1375 s	1385 sh	1380 s	1380 s	
1360 w	1360 m	1360 sh	1350 sh	1370 s	1365 vw	1275 w	
1295 w	1300 w	1284 s	1300 w	1300 w	1275 w	1265 w	
						1220 s	
1230 s	1258 w	1260 w	1275 w	1275 w			
	1242 w	1240 sh	1254 w	1228 w	1250 w		
1175 m	1180 m	1182 m	1175 m	1175 m	1175 m	1175 m	C—N stretch
. . .	. . .	. . .	. . .	1160 sh	. . .	1152 m	
1090 vs, b	1110 vs, b	1110 vs, b	1095 vs, b	1110 vs, b	1110 vs, b	1090 vs, b	ClO$_4^-$
1070 vs, b			1000 sh		1045 sh	1050 sh	

[a] A = $C_{16}H_{32}N_4$ (*trans* isomer). [b] Metallo complexes prepared by the reaction of I with the respective metal carbonates. [c] Prepared by means of reaction 1. [d] Abbreviations: s = strong, w = weak, m = medium, sh = shoulder, b = broad, sp = sharp, v = very. [e] Bands due to coordinated CO_3^{2-}.

water, so some special precautions were taken. Ethanolic solutions of anhydrous iron(II) perchlorate were prepared by treating the hydrated salt with 2,2-dimethoxypropane[10] and then diluting the solution with absolute alcohol. Anhydrous $[Fe(en)_3](ClO_4)_2$ was prepared from the ethanolic iron(II) solution by rapidly adding a slight excess of 98–100% ethylenediamine. The mixture was cooled with cold water, and the light brown crystalline precipitate was filtered and washed twice with absolute alcohol and once with ether. The solid was then dried in a stream of nitrogen.

Anhydrous $[Fe(en)_3](ClO_4)_2$ (40 g) was dissolved in 400 ml of dry acetone, and the solution was kept undisturbed at room temperature in a partly covered conical flask. Tiny transparent crystals started to form on the walls of the flask within 2 to 3 hr, and simultaneously a black precipitate (probably FeO) was formed. The crystals grew larger during the subsequent 36 hr while the supernatant solution turned very dark and became viscous. The crystals were filtered off, washed several times with acetone to remove the polymeric impurities, and finally separated from the black precipitate by decanting in the presence of ethanol; 28 g of the crystals (approximately 63% yield) was thus obtained. Pure white shiny plates can be obtained by recrystallizing the powdered crude crystals from hot aqueous methanol or hot aqueous ammonium hydroxide. The crude product may be used as the intermediate for the preparation of the metallo complexes, since recrystallization reduces the yield due to hydrolysis. The infrared spectra of the crude and recrystallized compounds were identical. We have observed that the yield of product is greatly diminished if the reactants are placed together in a tightly stoppered flask. On the other hand, no crystalline product is obtained if oxygen or air bubbled through the reactant mixture. The crude product is always found contaminated with varying amounts of iron oxide.

The melting point was not determined because of the explosive nature of the compound. However, it was observed that the crystals do not melt or explode when heated to 110°. *Anal.* Calcd for $C_{16}H_{34}Cl_2N_4O_8$: C, 40.0; H, 7.1; N, 11.7. Found: C, 40.5; H, 7.2; N, 11.7.

5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-dienenickel(II) Perchlorate $[Ni(C_{16}H_{32}N_4)](ClO_4)_2$. The $Ni(A)^{2+}$ complex was prepared by heating 50 ml of a 1:1 methanol–water mixture with an excess of nickel carbonate and 2 g of I on a steam bath for 5 to 10 min. The yellow solution thus formed was filtered from the unreacted nickel carbonate and evaporated to a small volume. On cooling the concentrated solution the yellow nickel complex crystallized. The product was recrystallized from hot water. *Anal.* Calcd for $C_{16}H_{32}Cl_2N_4O_8Ni$: C, 35.8; H, 6.0; N, 10.4. Found: C, 35.8; H, 6.1; N, 10.5.

Hexamethyl-1,4,8,11-tetraazacyclotetradecadienecopper(II) Perchlorates, $[Cu(C_{16}H_{32}N_4)](ClO_4)_2$. This complex was prepared by heating copper(II) carbonate with an excess of I as described above for the nickel complex. From the red solution thus obtained we were to crystallize both of the conformers $CuA_\beta{}^{2+}$ and $CuA_\alpha{}^{2+}$ identified by Curtis.[11] Approximately 80% of the product was the α isomer. The two isomers were identified by their color, spectra, and physical properties.

Chloroaquo-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-dienezinc(II) Perchlorate, $[Zn(C_{16}H_{32}N_4)(H_2O)Cl]ClO_4$. A solution of 3 g of zinc in 100 ml of 6 *N* HCl was neutralized with Na_2CO_3, and the resulting solution was heated with a slight excess of I on a steam bath for 5 min. The mixture was filtered hot, the colorless solution cooled, and absolute ethanol added to cause the white needle crystals to separate. The infrared spectrum of the solid exhibited typical O–H and ClO_4 absorption (Table I), and a solution of the complex gave a precipitate with $AgNO_3$. *Anal.* Calcd for $C_{16}H_{34}Cl_2N_4O_5Zn$: C, 38.6; H, 6.8. Found: C, 38.6; H, 6.7.

Carbonato-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-dienecobalt(III) Perchlorate, $[Co(C_{16}H_{32}N_4]CO_3)ClO_4$. A mixture of 2 g of $Na_3[Co(CO_3)_3]\cdot xH_2O$[12] and an excess of I in water was heated on a steam bath until the effervescence stopped (5 min). The dark red solution was filtered off and concentrated on the steam bath. On cooling slowly, large red crystals separated. The crystals were recrystallized from a minimum amount of water. *Anal.* Calcd for $C_{17}H_{32}ClN_4O_7Co$: C, 40.9; H, 6.4; N, 11.2. Found: C, 40.2; H, 6.6; N, 11.3.

5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-dienecobalt(II) Perchlorate, $[Co(C_{16}H_{32}N_4)](ClO_4)_2$. This complex was prepared both by means of the reaction between I and $CoCO_3$, analogous to preparations described above for nickel and copper, and by means of a variation of reaction 1. In either case oxygen must be rigorously excluded from the preparative solutions to prevent the formation of Co(III) complexes. Only the preparation by means of the "direct" reaction (1) will be described since this presented some unusual challenges.

Anhydrous $[Co(en)_3](ClO_4)_2$ was dissolved in dry acetone, and the solution stood under an atmosphere of nitrogen for 4 days. The

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(11) N. F. Curtis, Y. M. Curtis, and H. K. J. Powell, *J. Chem. Soc.*, 1015 (1966).

(12) H. F. Bauer and W. C. Drinkard, *J. Am. Chem. Soc.*, **82**, 5031 (1961).

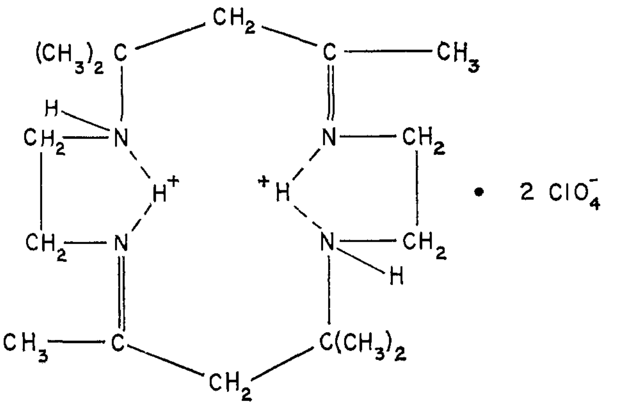
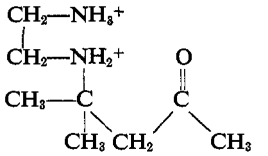


Figure 1. 5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene dihydrogen perchlorate (A·2HClO$_4$).

initial light pink color of the solution gradually grew darker and the solution became viscous. This dark viscous mixture was refluxed for 2 hr at 60–70°; then most of the acetone was distilled off under reduced pressure. The light brown crystals (II) which separated were washed several times with dry acetone and with absolute ethanol. This compound proved to be very reactive (*e.g.*, hydrolyzing rapidly in cold water) and showed a strong O–H stretching absorption near 3600 cm^{-1}. The elemental analysis seemed to agree best with a noncyclic Schiff base complex of Co(II). Further refluxing with acetone did not result in cyclization even in the presence of bases such as ethylenediamine, pyridine, or sodium ethoxide.

The crystalline material (II) was finely ground and treated with 1,1,1-trifluoroacetone and the suspension kept under a nitrogen atmosphere in a stoppered tube for several days. The brown color of the crystals gradually turned lighter and finally changed to yellowish brown within 5 days. These latter crystals were filtered, washed with absolute alcohol and ether, and dried under vacuum. The infrared spectrum was similar to that of the nickel complex (Table I) and showed no O–H absorptions. *Anal.* Calcd for $C_{16}H_{32}ClN_4O_8Co$: C, 35.7; H, 5.9; N, 10.4. Found: C, 35.2; H, 5.9; N, 10.0.

Hydrolysis Products. 4-(β-Aminoethylamine)-4-methylpentan-2-one Hydrobromide Hydroperchlorate (a). A 1-g portion of crude I was dissolved in 5 ml of concentrated HBr. When the filtered solution was evaporated at room temperature a pale white solid separated. This was washed with ethanol and ether and air dried. The dried product appeared to be a mixture consisting predominantly of a light colored crystalline portion with a shiny white amorphous fraction as the minor constituent. Since it proved to be difficult to separate the two fractions by recrystallization, they were separated by decantation with alcohol. The crystalline fraction was soluble in water, and the aqueous solution gave a white precipitate when mixed with AgNO$_3$. The infrared spectrum of this same crystalline fraction exhibited a typically strong ClO$_4^-$ absorption, and the partial elemental analysis agrees with the mixed anion formulation a. *Anal.* Calcd for $C_8H_{20}ClBrN_2O_4$: C, 29.8; H, 5.9. Found: C, 29.2; H, 5.7.



a

The amorphous fraction of the above mixture differed from structure a both in its empirical formula and infrared spectrum. This fraction was not further characterized.

On evaporating I twice with hot dilute HBr and then diluting the cold concentrated solution with several volumes of alcohol, we obtained pure white shiny crystals. These were identified as ethylenediamine dihydrobromide. *Anal.* Calcd for $C_2H_{10}Br_2N_2$: C, 10.8; H, 4.5; N, 12.6; Br, 72.0. Found: C, 11.2; H, 4.6; N, 12.6; Br, 71.7.

Reduction of I with NaBH$_4$. It is very difficult to prevent base hydrolysis of I during this reduction. We have succeeded in reducing I by (1) cooling in an ice bath a slurry of 1 g of I in 10 ml of methanol-water and (2) adding solid NaBH$_4$ to this mixture very slowly (less than 0.05 g at a time). The mixture should be stirred vigorously during the addition of NaBH$_4$.

Results and Discussion

The reaction of $[Fe(en)_3](ClO_4)_2$ with acetone proceeds very rapidly and seems complete within a few hours. However, the formation of the Schiff base dihydrogen perchlorate (I) appears to be very sensitive to the reaction conditions, particularly to the presence of water or air. The purified compound obtained by recrystallization from hot aqueous methanol does not contain any iron. The molecular weight determined for I was 456 which agrees reasonably well with the theoretical value of 480 for $C_{16}H_{34}N_4Cl_2O_8$. Since metallo complexes formed from I seem to correspond predominantly to Curtis' MA^{2+} complexes,[11] and in view of other evidence discussed below, we suggest that the Schiff base dihydrogen perchlorate (I) is predominantly of the structure A·2HClO$_4$[13] (Figure 1). Compound I is insoluble in hot and cold water, and the solid hydrolyzes relatively slowly in boiling water, dilute acids, and dilute bases. The compound is rapidly decomposed by strong alkalies. Decomposition of I with concentrated HBr showed that several stages of hydrolysis are possible. Two separate products were isolated and identified by elemental analysis and infrared spectra: (1) a completely hydrolyzed product identified as ethylenediamine dihydrobromide and (2) a partially hydrolyzed product having a molecular formula and infrared spectrum agreeing with structure a. $\nu_{C=O}$ occurred at 1710 cm^{-1}. This product would of course be expected in the partial hydrolysis of A·2HClO$_4$. Ethylenediamine dihydrobromide can be isolated from the further hydrolysis of a.

We have attempted to titrate aliquots of I dissolved in 50% methanol–water with standard NaOH and standard HCl. In the titration with HCl, I exhibited no basic properties whatsoever. In the titrations with NaOH there was evidence of a buffering effect over the range of pH 8.5 to 10.5; however, the midpoint of the buffer range depended on the concentration of NaOH (becoming more basic at higher [NaOH]), and there was no effective equivalence point. Evidently I can behave as a very weak acid, and the base hydrolysis proceeds rapidly enough and extensively enough that we have not been able to estimate the extent of acid dissociation (the extent of dissociation was less than 10% in the neutral solution). We have also examined the pmr spectra in a dilute basic (with Na$_2$CO$_3$) D$_2$O solution of I and find that the spectra are very complex and vary with time, indicating that several species are present.

The preparation of the NiA^{2+} and CuA^{2+} complexes seems to confirm the structure A·2HClO$_4$ for the predominant species present in I. We have not been able to detect any of the NiB^{2+} complex when I is used as the preparative intermediate. The hydrolyzed product (a) also reacts with Ni(II) and Cu(II) to give respectively NiA^{2+} and CuA^{2+}. This is possible by the condensation of 2 moles of a around a Ni^{2+} "template."

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(13) In order to keep our notation consistent with that used by Curtis,[11] we will use "A" to denote 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-5,11-diene in which the two *gem*-dimethyl groups can be regarded as being *trans* to one another. The geometrical isomer of A in which the *gem*-dimethyl groups are *cis* to one another will be denoted by B.

The infrared absorption frequencies of I and the Ni(II), Cu(II), Zn(II), and Co(III) complexes prepared from it are compared in Table I with the infrared absorption frequencies of the Ni(II), Cu(II), and Co(II) complexes prepared by means of the general reaction 1. Significant differences in the spectra of I and its metallo derivatives occur only in the regions of the N-H absorptions. The strong broad band at 3150 cm^{-1} assigned to ν_{N-H} becomes sharper and less intense and increases in frequency (to approximately 3200 cm^{-1}) in the metallo derivatives. Secondly, a strong band at 1544 cm^{-1} assigned to the antisymmetric NH_2 deformation occurs in I but does not appear in the spectra of any of the metallo complexes. That both these absorptions are associated with N-H vibrations has been substantiated by the observation that an appropriate isotopic shift is observed (see Figure 2) when I is deuterated ($\nu_{N-H}/\nu_{N-D} = 1.36$). Unfortunately, the exact magnitude of the shift in the deformation band could not be accurately ascertained because of the presence of the very intense broad perchlorate absorption in the 1200–1000-cm^{-1} region of the spectrum where the ND_2 deformation frequency would be expected to occur.

Broadening of the infrared bands and increases in intensity as well as shifts to lower frequency are all characteristics of hydrogen bonded N-H stretch.[14] In the deuterated analog of I two broad well-resolved bands were observed at 2325 and 2155 cm^{-1} (ν_{N-D}). The lower frequency band would probably be associated with a N-D$^+$ stretch which in the case of I would be obscured by the C-H stretching absorptions. The presence of the strong antisymmetric δ_{NH_2} at 1544 cm^{-1} in I and its disappearance in the complexes further support a N-H$^+$-N hydrogen bond[15] as in A′.

The BH_4^- reduction of I gives a white crystalline solid whose infrared spectrum is nearly identical with the infrared spectrum of the hydrogen perchlorate of $C_{16}H_{36}N_4$. The latter compound was prepared by means of the hydrogenation of $Ni(C_{16}H_{32}N_4)^{2+}$.[16]

It seems reasonable to attribute much of the stability of I to N-H$^+$-N hydrogen bonding between the acidic protons and the central nitrogen atoms which, together with the geometrical constraints of the macrocyclic dien system, would combine to protect the azomethine linkage from rapid hydrolysis. Examination of molecular models indicates that the atomic distances are favorable for an N-H-N type of bonding as shown in Figure 1, whether the two >C=N— bonds are *trans* or *cis* (*i.e.*, whether the isomer is A or B) to each other. The infrared spectrum in the region of the N-H vibrations (Table I) seems to be consistent with hydrogen bonding and with the existence of an NH_2^+ group in the molecule. Hydrogen bonding involving all four hydrogen atoms seems sterically impossible.

The reaction of I with metal ions, forming the metallo complex by the displacement of the two protons of $A \cdot 2HClO_4$, may be quite general since we have been able to prepare the analogous Cu(II), Co(II), Co(III), and Zn(II) complexes in this manner. It is interesting to note that the formation of the protonated Schiff base $A \cdot 2HClO_4$ and the displacement of the protons by metals ions in basic solution has very striking analogs in the much more complicated porphyrin[8] and phthalocyanine[17] systems. It is also of particular interest that the stability of $A \cdot 2HClO_4$ cannot depend on a network of conjugated double bonds.

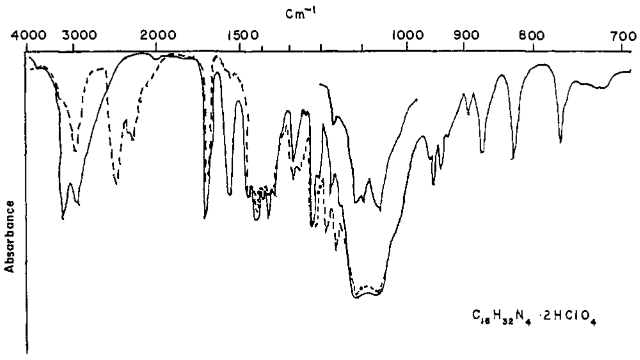

Figure 2. Infrared absorption spectra of I: ———, spectrum of compound; ----, spectrum after equilibration with D_2O.

The visible absorption spectra of I and of several metallo complexes prepared from it are presented in Table II. The ultraviolet absorption bands of I, CuA^{2+}, $CoACO_3^+$, and $ZnACl(H_2O)^+$ are tentatively assigned by analogy with similar bands occurring in NiA^{2+}.[11] We have represented the Zn(II) complex as hexacoordinate, but we have not substantiated this geometry. If the Zn(II) complex is hexacoordinate, the species in aqueous solution is undoubtedly $ZnA(OH_2)_2^{2+}$ under the conditions of our determination of the absorption spectrum. The Ni(II) and Cu(II) spectra agree well with previously published data[4,11] for spectra of these complexes when they are prepared by means of the direct reaction (1). The extinction coefficient cited for I may not be very reliable because of the hydrolysis reactions; however, the position of the band maximum should be correct.

Table II. Absorption Spectra in Aqueous Solution[a]

	Band assignments[b]		
	Metal ion	C=N	Charge transfer
$[NiA](ClO_4)_2$[c]	23.2 (95)	36.2 (5100)	46.8 (17,000)
$[CuA](ClO_4)_2$[c]	20.1 (106)	40.2 (5600)	>50 (>11,000)
$[CuB](ClO_4)_2$[c]	20.4 (115)	40.6 (6400)	52.6 (~11,400)
$[CoACO_3]ClO_4$[c]	20.0 (121)		41.2 (16,200)[d]
	28.6 (135)		~52 (sh, ~10^4)
$[ZnACl(H_2O)]ClO_4$[c]		43.5 (620)[d]	>50 (>10^3)
$[C_{16}H_{34}N_4](ClO_4)_2$		47.5 (450)[d,e]	>50 (>500)[d,e]

[a] At 25° in neutral solution; band maxima in 1000 cm^{-1}, molar extinction coefficients in parentheses. [b] Band assignments follow those made by Curtis.[11] [c] Metallo complexes prepared from I. [d] Assignment of these bands is uncertain. [e] Determined in aqueous methanol. The actual extinction coefficient may be higher than the value cited because of hydrolysis of I. One of the initial hydrolysis products exhibits an absorption maximum at 40.2 × 10^3 cm^{-1}.

The metal ion may play an essential role as a "template" in the formation of this type of macrocyclic Schiff bases;[2,16] however, the differences between the four metals we have worked with are quite striking. In the case of Ni(II) and Cu(II) the identifiable materials

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(14) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bonds," Reinhold Publishing Corp., New York, N. Y., 1960.

(15) L. J. Bellamy, "Infrared Spectra of Complex Molecules," Methuen, London, 1958.

(16) N. F. Curtis, *J. Chem. Soc.*, 2644 (1964).

(17) P. A. Barrett, C. E. Dent, and R. P. Linstead, *ibid.*, 1719 (1936).

isolated from reaction 1 are the metallo complexes (either of the A or B isomer or of some of the intermediate, noncylic species,[14] while with Fe(II) under identical preparative conditions a mixture of iron oxide and the protonated Schiff base (I) are obtained. It is presumed that the iron(II) complex exists as an intermediate in the formation of I; however, we have thus far failed in our attempts to prepare an unequivocal $Fe(C_{16}H_{32}N_4)^{2+}$ complex. In the case of Co(II) considerable difficulty has been experienced with the direct reaction (1). The major sources of difficulty in this latter case appear to arise from the insolubility of cobaltous hydroxides and the hydrolysis or polymerization of the partly condensed products. In some of our preparations involving the reaction of $Co(en)_3(ClO_4)_2$ with acetone in the presence of trifluoroacetone or 2,2-dimethoxypropane, we have found that the macrocyclic Schiff base dihydrogen perchlorate (I) occurs as an important reaction product.

Although the mechanism of reaction 1 is unknown and the factors which govern the formation of the products eventually isolated are not clearly established, it is apparent from our experience with reaction 1 for Ni(II), Cu(II), Co(II), and Fe(II) that both the yield and the nature of the products depend strongly on such thermodynamic quantities as the solubility of the metal oxides and hydroxides, the insolubility of I, and possibly the thermodynamic stability of the $M(en)_3^{2+}$ and MA^{2+} complexes. Thus the $Ni(C_{16}H_{32}N_4)^{2+}$ and the $Cu(C_{16}H_{32}N_4)^{2+}$ complexes can be obtained in good yields, and the preparations are not complicated by the formation of the metal hydroxides or oxides. In the case of Co(II) the $Co(C_{16}H_{32}N_4)^{2+}$ complex can only be isolated if water is rigorously excluded and thus the hydroxide formation prevented. And finally $Fe(C_{16}H_{32}N_4)^{2+}$ has not been identified as a product of reaction 1, but rather we obtain iron oxide and I. Even in the case of Cu(II) and Ni(II), where insoluble metal oxides or hydroxides do not form, reaction 1 generally gives dark polymeric side products if water is not rigorously excluded. However, if these reactions are run in the presence of such scavengers for water as 1,1,1-trifluoroacetone or 2,2-dimethoxypropane, the formation of dark polymeric materials is repressed and the yield of the $(C_{16}H_{32}N_4)^{2+}$ complexes is increased. In the case of Cu(II) the yield of $Cu(C_{16}H_{32}N_4)^{2+}$ is increased from about 10% in acetone to about 80% in acetone solution containing 2,2-dimethoxypropane or 1,1,1-trifluoroacetone.

A large number of macrocyclic Co(III) complexes have now been prepared from I, either by preparing $CoA(CO_3)^+$ as an intermediate or by oxidizing CoA^{2+} in the presence of the appropriate ligands. The details of these preparations as well as the characterization and chemistry of the Co(III) complexes will be the subject of a later communication.[18]

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[18] NOTE ADDED IN PROOF. N. F. Curtis and R. W. Hay have very recently reported (*Chem. Commun.*, 524 (1966)) that the macrocyclic Schiff base dihydrogen perchlorate I is readily obtained from the reaction of ethylenediamine hydrogen perchlorate and acetone.